

A CONTRIBUTION
TO THE STUDY OF
DOUBLE SALTS IN WATER SOLUTION.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY.

—BY—

EBENEZER MACKAY

1896

EASTON, PA.:
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INTRODUCTION.

If a solution of a mixture of two salts having a common ion be subjected to crystallization, the two salts may crystallize out separately or crystals may form containing both. In the latter case two modes of separation are to be distinguished, according as the crystals formed are of variable or of constant composition. When of variable composition they are mixed crystals, or isomorphous mixtures. When the constituent salts are present in constant molecular proportions, the crystalline compound is a double salt. The constancy of composition of the crystals of a double salt raises the question whether the double salt is present as such in solution or is first formed only at the moment of crystallization.

The question of the existence of double salts in solution has attracted the attention of many investigators, and a variety of methods have been employed in the investigations. The chief methods, classified according to the phenomena or properties investigated, may be grouped according as they relate (a) to diffusion; (b) to thermal changes; (c) to volume changes; (d) to solubility; (e) to electrical properties; or (f) to cryoscopic behavior.

Graham,¹ in his classic researches on diffusion, studied incidentally the diffusion of a few double salts, among them alum and the double sulphate of magnesium and potash. He found that the constituents of the former were present in the diffused liquid in a proportion different from that in the alum itself, and inferred that the alum in solution was at least partially decomposed. With regard to the latter salt, he found that the amount of the double salt which diffused was equal to the sum of the amounts diffused of its constituents taken separately; and he concluded that this double salt was not decomposed in solution. As Graham had not determined the proportions in which the constituents of the double sulphate of magnesium and potash had diffused, but only the total amount of diffusion, his work was repeated by Marignac,²

¹ Phil. Trans., 1850, I.

² Ann. chim. phys., [5], 2, 546, (1874).

who concluded from an extensive series of observations that there is no difference between mixtures of salts capable of forming double salts and those in which no union can take place. He inferred that double salts are only formed at the moment of crystallization. The work of van der Wal,¹ who diffused alums and other double sulphates, and of Ingenhous,² who investigated barium acetate and similar salts, lead to the same result. The latter found that the constituents of the salts examined diffused, not in the proportion in which they exist in the double salt, but nearly as if diffused separately. Rüdorff,³ following the same mode of investigation, divided double salts into two classes, according as their constituents were found in the diffusate in the same proportion as in the double salt or in a different proportion. Rüdorff also investigated the relation between dissociation and concentration and found that, until near the point of saturation, the two were independent; but that if crystals of the double salt were placed upon the diaphragm so as to maintain saturation, the proportion of the constituents diffused much more nearly approached their proportion in the double salt. He inferred that molecular compounds exist in fully saturated solutions. This inference was criticised by Ostwald,⁴ and later by Trevor,⁵ on the ground that the effect observed was due to the more rapidly diffusing constituent becoming relatively less concentrated in the diffusion vessel; and the latter undertook a series of experiments confirming this view. On the other hand, E. Fischer and Schmidner,⁶ by allowing a saturated solution of ferrous ammonium sulphate to diffuse upwards through rolls of filter paper inside a glass tube, found the proportion of the constituents in the filter paper the same as in the double salt.

In the field of thermochemistry, conclusions as to the existence of double salts in solution are based upon a principle stated by Berthelot⁷ as follows: "Everything indicates that double salts formed with a feeble disengagement of heat are to be regarded as separated in greater part into their constitu-

¹ Inaugural Dissertation. Leyden, (1869).

² Ber. d. chem. Ges., **12**, 1678, (1879).

³ Ber. d. chem. Ges., **21**, 4; **21**, 1882; **21**, 3044, (1888); **23**, 1846, (1890).

⁴ Ztschr. phys. Chem., **3**, 601, (1889).

⁵ Ztschr. phys. Chem., **7**, 468, (1891).

⁶ Ann. chem. (Liebig), **272**, 156, (1892).

⁷ Méc. Chem., **II**, 324.

ents by water." On this principle Favre and Valson,¹ finding that the constituents of the alums evolved no heat on mixing, concluded that the latter come into existence only through crystallization. Graham² had previously made similar experiments with other double sulphates, reaching the same results. Graham³ found, on the other hand, that thermal changes occurred when solutions of the chlorides of mercury and ammonium were mixed. Similarly, Berthelot⁴ found that in general the thermal changes on mixing solutions of the halogen salts of mercury and potassium were not equal to the sum of the thermal changes for the component salts, and concluded that the existence of double salts in such solutions was thereby proved.

Of importance in their bearing upon the question are also the volume changes which occur when salt solutions are mixed. Kremers,⁵ finding no change of volume on mixing solutions of salts capable of forming double salts, inferred that no double salts existed in solution, on the ground that chemical changes are known to be accompanied by changes of volume frequently large. Favre and Valson⁶ drew a similar conclusion from the fact that the density of a solution of potassium cupric sulphate is the mean of the densities of its constituents. Gerlach,⁷ however, noticed a slight contraction of volume in the case of the alums on mixing solutions of their constituents, which became more marked with increasing concentration; and upon this and other grounds he inclined to the belief that these double salts exist as such in their solutions. The conclusions of Groshans⁸ from observations on double chlorides and sulphates confirmed those of Kremers.

Researches upon the solubility of salt mixtures, especially upon the states of equilibrium in solution when two salts capable of forming a double salt are dissolved together, have contributed largely to a knowledge of the state of double salts in solution. Mulder⁹ drew from the work of Kopp¹⁰ and

¹ Compt. rend., **74**, 1165, (1872).

² Phil. Mag., **24**, 401, (1844).

³ Pogg. Ann., **98**, 58, (1856).

⁴ Ztschr. anal. Chem., **28**, 485, (1889).

⁵ Jahrsb. Chem., 1864, 92; 1866, 65.

⁶ Phil. Mag., **20**, 539, (1842).

⁷ Ann. chim. phys., [5], **29**, 198, (1883).

⁸ Compt. rend., **77**, 907, (1873).

⁹ Des Dissolutions Aqueuses, 2-7.

¹⁰ Ann. chem. (Liebig), **34**, 260, (1840).

others, extended by researches of his own, the conclusion that well-defined double salts exist in saturated solutions of salt mixtures. This conclusion was founded upon the observation that in such solutions, saturated with respect to each component, the salts are often found in simple molecular proportions. Some researches of Rüdorff¹ seemed to lead to a different conclusion. These, however, have been otherwise interpreted by Trevor.² The studies in equilibrium of Ditte³ on the double iodide of lead and potassium ($\text{PbI}_2 \cdot \text{K}_2\text{I}_2 \cdot n\text{H}_2\text{O}$), of Roozeboom⁴ on astrakanite, of Meyerhoffer,⁵ Vriens,⁶ Schreinemaker,⁷ and van der Heide⁸ have led to the general result that there are certain limits of temperature outside of which double salts are capable of existing in their solutions.

From van't Hoff's extension of the gas laws to solutions Nernst⁹ deduces the consequence that if to a saturated salt solution a solution of another salt having a common ion be added, the solubility of the former salt is decreased and a part of it precipitated. On examining certain cases in which the solubility of the first salt is increased under the conditions stated, Le Blanc and Noyes¹⁰ succeeded in showing that the apparent exceptions were due to the formation of double salts in solution. To the same cause Rose¹¹ attributed those cases in which a salt is found to be more soluble in the solution of another salt than in water. The view that the solution of silver chloride in ammonia is accompanied by the formation of a double salt in the solution has been confirmed by Bodländer.¹²

The application of electrolysis to a study of the state of double salts in solution was made early in the present century by Porret,¹³ who found that when potassium ferrocyanide was electrolyzed, alkali appeared at the negative pole, while oxide of iron and prussic acid appeared at the positive. The work of Daniell and Miller¹⁴ on the same salt, extended by Hit-

¹ Pogg. Ann., **148**, 558, (1873).

² *Loc. cit.*

³ Ann. chem. phys., [5], **24**, 226 (1881).

⁴ Ztschr. phys. Chem., **2**, 513, (1888); **12**, 359 (1893).

⁵ Ztschr. phys. Chem., **3**, 336, (1889).

⁶ Ztschr. phys. Chem., **7**, 194, (1891).

⁷ Ztschr. phys. Chem., **9**, 57, (1892); **11**, 289, (1893).

⁸ Ztschr. phys. Chem., **12**, 416, (1893).

⁹ Ztschr. phys. Chem., **4**, 372, (1889).

¹⁰ Ztschr. phys. Chem., **6**, 385, (1890).

¹¹ Pogg. Ann., **82**, 545, (1851).

¹² Ztschr. phys. Chem., **9**, 730, (1892).

¹³ Phil. Trans., 1814, 527.

¹⁴ Pogg. Ann., **64**, 18, (1845).

torf¹ to many other double salts, lead to the view that double salts are of two classes: (1) those which do not exist as such in solution, and (2) those containing a metal combined with a complex radical, which are capable of existing in water solution undecomposed. In the nomenclature of Ostwald² the latter are "complex salts," the term "double salt" being applied to members of the first class only. To the complex salts he refers potassium ferrocyanide and analogous salts; to the double salts he refers the alums. Between these extreme types various degrees of dissociation may exist.

Researches upon the electrical conductivity of double salts and salt mixtures are numerous. Of chief importance in the present connection are those of Bouchotte³ and Paalzow⁴ on sulphates of copper and zinc in common solution; of Svenson⁵ on alums, of Grottrian⁶ on the salt K_2CdI_4 , of Freund,⁷ Bender,⁸ Bouty,⁹ Arrhenius,¹⁰ and Chroustchoff and Packhoff¹¹ on mixtures of electrolytes; of Klein¹² on mixtures and double salts; of Wershoven¹³ on dilute solutions of cadmium salts; and of Kistiakowsky¹⁴ on dilute solutions of "complex" salts. The results of these investigations, in so far as they refer to the dissociation of double salts, agree in showing that with increasing dilution, many double salts rapidly approach the condition of a simple mixture. For concentrated solutions, Klein, who compared the conductivities of salt mixtures capable of forming double salts with that of those whose constituents were without mutual chemical action, showed that in the former case the difference between the conductivity of the mixture and the mean conductivity of its constituents was much greater than in the latter case; and he inferred that in concentrated solutions there is only partial dissociation. For complex salts Kistiakowsky found that even in very dilute solutions their complex ions remained undecomposed. The conductivity method has also been applied by

¹ Pogg. Ann., **106**, 513, (1859).

² Compt. rend., **62**, 955, (1866).

³ Beibl., **2**, 46, (1878).

⁴ Wied. Ann., **7**, 44, (1879).

⁵ Ann. chim. phys. [6], **3**, 433, (1884): **14**, 74, (1888).

⁶ Biebl., **9**, 437, (1885): Wied. Ann., **30**, 51, (1887).

⁷ Compt. rend., **108**, 1162, (1889).

⁸ Ztschr. phys. Chem., **5**, 481, (1890).

² Ztschr. phys. Chem., **3**, 596, (1889).

⁴ Pogg. Ann., **136**, 489, (1869).

⁶ Wied. Ann., **18**, 177, (1883).

⁸ Wied. Ann., **22**, 179, (1884).

¹² Wied. Ann., **27**, 151, (1886).

¹⁴ Ztschr. phys. Chem., **6**, 97, (1890).

Le Blanc and Noyes,¹ by Bodländer² and others to indicate the existence of double salts in the respective cases studied.

The application of the freezing-point method has been especially studied by Raoult.³ By comparing the lowering given by double salts with the sum of the lowerings of their constituents, he concluded that certain double sulphates, including the alums, are entirely dissociated, while other salts examined, as the chlorides of mercury, go into solution with but partial decomposition.

From the foregoing summary it will be seen that the classification of double salts into two groups according as they are wholly or but partially decomposed by water is well established so far as regards dilute solutions, but that in more concentrated solutions the evidence is not sufficient to regard the classification as final. The present investigation has been undertaken with the object of obtaining such further data as may justify more definite conclusions. The work has been confined to some alums as representatives of an extreme type of dissociation, and to one member of the dissociated class of double chlorides. The results reached are based upon a comparison of the electrical conductivity and cryoscopic behavior of the double salts with that of their constituent salts, with a view to determining to what extent the solutions of the double salts correspond to mixtures.

Conductivity Apparatus.

The measurements of conductivity were made by the Kohlrausch method, using a Wheatstone bridge, induction coil and telephone. The special form of the apparatus used was that described by Ostwald.⁴ The bridge wire was calibrated by the method of Strouhal and Barus.⁵ Conductivity cells of the Arrhenius form were employed with electrodes at different distances, one for solutions less than 0.001 normal, the other for those more dilute. In this way satisfactory tone minima were obtained throughout a wide range of dilution. The temperature selected for the measurements was, in general, 25°. By means of a thermostat the tempera-

¹ *Loc. cit.*

² *Loc. cit.*

³ *Compt. rend.*, **99**, 914, (1884).

⁴ *Ztschr. phys. Chem.*, **2**, 561, (1888).

⁵ *Wied. Ann.*, **10**, 326, (1880).

ture was easily kept constant under ordinary conditions to within 0.1 degree.

Solutions.

The flasks and pipettes used in making up solutions were calibrated for a temperature of 20°, the former by the apparatus devised by Professor Morse of this laboratory and Blalock,¹ the latter by weighing in successive portions the water delivered at a known temperature.

The solutions were prepared at 20° and standardized by analysis of a measured volume except in the few cases in which the concentration could be known from the weight of the salt dissolved.

As the character of the water effects appreciably the conductivity of solutions more dilute than 0.02 normal, the water used was prepared by redistilling ordinary distilled water successively from solutions of alkaline and acid permanganate of potash, employing a block tin condenser. The water so prepared gave, in general, a conductivity at 25° varying from 1.5 to 2×10^{-6} mercury units. The conductivity of the water used was measured for each series of determinations, and the correction applied.

Conductivity Measurement.

In making a series of conductivity measurements the general method adopted was to make up from the original solution, standardized by analysis, a solution which was a simple multiple or fraction of normal; 25 or 50 cc. of this solution were then measured with a pipette into the cell and successive solutions prepared from this in the cell itself by withdrawal of a measured portion and addition of an equal volume of water. As a check upon errors of dilution, a series of solutions were made up independently in measuring flasks at intervals corresponding to four or more dilutions in the cell. These solutions were used as standards, and when the conductivity of the cell dilution differed a proportional correction was applied, in the manner indicated by Kohlrausch,² to the members of the series immediately preceding, provided this correction did not exceed 0.5 or 0.75 per cent; when it did,

Am. Chem. J., 16, 479, (1894).

² Wied Ann., 26, 184, (1885).

the measurements were repeated. The cell was standardized at frequent intervals with 0.02 normal potassium chloride.

Certain cases occurred in which the solutions were found to be unstable at great dilutions. In these cases the check solutions were made up immediately before measuring their conductivity.

A Method of Titrating Aluminium.

As the necessity of standardizing solutions containing aluminium often occurred in the progress of the work, a reliable and convenient method of titration became desirable. None of the methods described in the literature seem to have proved satisfactory. That of Bayer¹ by titration of sodium aluminate with sulphuric acid, using litmus and methyl orange as indicators, is described as a "tedious, hot and uncertain process;"² while, in the method of Lunge,³ the ratio of the acid consumed to the aluminium has been the subject of much discussion.

After some unsuccessful attempts with barium hydroxide, the following method of titration with ammonia, using litmus as an indicator, was finally adopted, and has been found to give fair results: A measured volume of the alum solution is heated nearly to boiling, and the sulphate precipitated with barium chloride avoiding a large excess. A 0.05 normal solution of ammonia is now added slowly and with constant shaking until the solution reacts weakly alkaline. The change of color is very gradual and could not be used in direct titration. The solution is now diluted to a known volume, the whole operation being conducted in a 100 cc. flask, and allowed to stand some hours, until most of the precipitate has settled. Some of the solution is then decanted off and passed through a small filter, the first part of the filtrate being thrown away to avoid change in concentration. 50 cc. of the filtrate are next measured off, a few drops of litmus again added and the solution titrated to color with standard hydrochloric acid.

A solution of potassium alum titrated in this way gave the following results:

¹ Ztschr. anal. Chem., **24**, 542, (1885). ² E. B., Ztschr. anal. Chem., **25**, 183, (1886).

³ Ztschr. angew. Chem., **227**, 293, (1890).

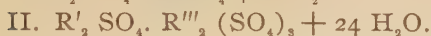
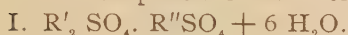
I.	1 cc.	solution contains	0.0948	gram alum.
II.	1 cc.	" "	0.0946	" "
III.	1 cc.	" "	0.0945	" "
IV.	1 cc.	" "	0.0944	" "
V.	1 cc.	" "	0.0944	" "
Mean,				0.0945 " "

The results of a gravimetric analysis by precipitation of the sulphate with barium chloride gave 0.09486 gram alum per cc.

I.

Alums.

Double sulphates conform to one of two types :



The alums, representing the latter type, form a group whose members are united by the closest analogies. Although taken by Rose¹ as the chief representatives of a class of double salts not easily decomposed by water, since he found that repeated crystallizations gave rise to no decomposition, later investigators, as Ostwald and Raoult, regard them as types of extreme dissociation. Any conclusions reached, therefore, with regard to the alums from this point of view become immediately applicable to a large group of double salts.

Conductivity Results.

As no conductivity data at 25° for sufficiently concentrated solutions of the constituents of the alums were available, measurements were made for potassium sulphate, aluminium sulphate and chromium sulphate.

Potassium Sulphate.

The salt, purified by repeated crystallizations, was dried to constant weight in an air-bath, and solutions made up from a weighed amount of the dry salt.

In the following tables conductivities are expressed in "molecular conductivity" units as defined by Ostwald,² instead of in "equivalent molecular" units, in order to facilitate the comparison of the conductivities of solutions containing

¹ Pogg. Ann., **82**, 545, (1851).

² Lehrbuch der allg. Chem., **2**, 621.

equal numbers of gram-molecules per litre but of different concentration expressed as normal.

The symbols, μ_{v15° , μ_{v25° , denote respectively the molecular conductivities at 15° and 25° , the numbers in the columns being multiplied by 10^7 .

The only direct measurements at 25° available for comparison are those of Walden,¹ which give by interpolation a very satisfactory agreement. Walden's results are as follows :

Litres per gram-molecule.		μ_{v25° .	
64.0		232.2	
128.0		246.0	
256.0		256.8	
512.0		265.4	
1024.0		272.8	
2048.0		278.6	

K_2SO_4 [174.34].			
Gram-molecules per litre.	Litres per gram-molecule.	μ_{v15° .	μ_{v25° .
0.333	0.3		157.4
0.25	4.0	134.7	167.9
0.2175	4.6052		170.2
0.10855	9.2104		186.9
0.1	10.0	148.2	187.0
0.05427	18.4208		202.8
0.05	20.0	162.9	205.1
0.0333	30.0	167.2	213.9
0.025	40.0	171.7	220.3
0.01666	60.0	179.4	229.1
0.005	200.0	200.7	252.4
0.0025	400.0		262.2
0.0005	2000.0		276.5
0.00025	4000.0		281.9
0.00005	20,000.0	237.8	279.6

Aluminium Sulphate.

The ordinary chemically pure aluminium sulphate was found to contain considerable quantities of sodium. The aluminium sulphate used was prepared from pure potassium alum. The aluminium was precipitated as hydroxide by ammonia, and the precipitate washed until it was found to be entirely free from potassium and ammonia. The washing was effected by boiling the precipitate with large quantities

¹ Ztschr. phys. Chem., 2, 49, (1888).

of water, allowing it to settle and successively decanting and filtering. This treatment was repeated a dozen or fifteen times. The pure aluminium hydroxide was dissolved in sulphuric acid in slight excess, as indicated by methyl orange, and the excess of acid removed by repeated precipitation of the salt with alcohol, the last traces of alcohol being removed by heating in an air-bath. The salt so obtained was in the form of a light powder and answered every test of purity. Analysis gave the following results :

	Calculated for $\text{Al}_2(\text{SO}_4)_3$.	Found.
Al	0.0479	0.048
SO_4	0.2548	0.255

Analysis of the standard solution gave :

I. 0.044706 gram $\text{Al}_2(\text{SO}_4)_3$ per cc.

II. 0.044778 gram $\text{Al}_2(\text{SO}_4)_3$ per cc.

Mean, 0.04474 gram $\text{Al}_2(\text{SO}_4)_3$ per cc., equivalent to 0.1307 gram-molecules per litre.



Gram-molecules per litre.	Litres per gram-molecule.		I. $\mu_v 15^\circ$.	II. $\mu_v 25^\circ$.	Mean.
0.21715	4.6052		105.7		
0.10855	9.210	107.7	130.3		
0.06666	15.0		148.2	148.5	148.3
0.05427	18.4208		153.6		
0.03333	30.0	139.1	172.5	172.7	172.6
0.016666	60.0		202.3	202.1	202.2
0.003333	300.0	243.6	300.4	300.8	300.6
0.001666	600.0		359.5	358.6	359.0
0.0005	1999.9	382.4			
0.0003333	3000.0		530.0	531.7	530.8
0.00025	3999.9	447.4			
0.0001666	6000.0		611.6	611.4	611.5
0.00003333	30000.0		806.1	809.1	807.6
0.000025	40000.0	678.4			
0.0000166	60000.0		869.4	869.4	869.4
0.0000125	80000.0	708.7			
0.00000625	160000.0	715.2			

These results for aluminium sulphate show a good agreement with Walden's measurements of dilute solutions at the same temperature.

Chromium Sulphate.

The chromium sulphate used was a specimen prepared under the direction of Professor Renouf of this laboratory. The process consisted in the reduction of chromic acid with ether under a bell-jar, filtration of the solidified crystalline mass with the aid of a pump, and careful drying of the product on plates of unglazed porcelain.¹

A concentrated solution of the salt was prepared. To diminish errors of analysis, the solution standardized was prepared from the original by diluting one volume to twenty. Analysis gave :

I. 0.007426 gram $\text{Cr}_2(\text{SO}_4)_3$ per cc.

II. 0.007410 gram $\text{Cr}_2(\text{SO}_4)_3$ per cc.

Mean, 0.007418 gram $\text{Cr}_2(\text{SO}_4)_3$ per cc.

Hence the original solution contained 0.3779 gram-molecules per litre.

The conductivity values obtained by Walden² differ widely from those in the following table for the conductivity of chromium sulphate. A comparison of a few approximately corresponding dilutions will show the extent of the difference. Column 1 gives Walden's values reduced to molecular conductivity units ; column 2, those from the following table for chromium sulphate at the same temperature :

Column 1.	Column 2.
$\mu_v 25^\circ = 378.0$ ($v = 192$)	$\mu_v 25^\circ = 288.2$ ($v = 200$)
439.2 ($v = 384$)	346.5 ($v = 400$)
589.2 ($v = 1536$)	558.2 ($v = 2000$)
669.6 ($v = 3072$)	

If the mean be taken of the conductivity values obtained by Walden for chromium sulphate and those corresponding for potassium sulphate, it leads to values for the conductivity of potassium chrome alum greatly in excess of those obtained in the present investigation.

The conductivity measurements for chromium sulphate are shown in the following table :

¹ Renouf : *Inorganic Prep.*, p. 78.

² *Ztschr. phys. Chem.*, 1, 541, (1887).

$\text{Cr}_2(\text{SO}_4)_3$ [392.58].

Gram-molecules per litre.	Litres per gram-molecule.	μ_{v15° .	μ_{v25° .
0.333	3.0		94.2
0.25	4.0	86.2	107.3
0.1	10.0		139.0
0.05	20.0	132.3	162.7
0.025	40.0		190.7
0.005	200.0	233.2	288.2
0.0025	400.0		346.5
0.0005	2000.0		558.2
0.00025	4000.0		671.2

Potassium Aluminium Alum.

The salt was purified by repeated crystallizations, and was found to be free from iron, sodium and ammonia. A solution was prepared approximately saturated at 20° . The solution was standardized by precipitation of the sulphuric acid with barium chloride. The results of analysis were:

I. 0.0952 gram $\text{KAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

II. 0.0948 gram $\text{KAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

III. 0.09458 gram $\text{KAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

Mean, 0.09486 gram $\text{KAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc. of solution, or equivalent to 0.19995 gram-molecules per litre.

The conductivity obtained is shown in the following table:

 $\text{KAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ [474.41].

Gram- molecules per litre.	Litres per gram- molecule.	I.	II.	Mean
		μ_{v25° .	μ_{v25° .	
0.19995	5.0012	133.9	133.9	133.9
0.125	8.0	149.2	149.2	149.2
0.05	20.0	178.3	178.3	178.3
0.025	40.0	202.5	202.5	202.5
0.005	200.0	268.2	269.9	269.0
0.0025	400.0	304.2	306.3	305.2
0.0005	2000.0	407.0	406.8	406.9
0.00025	4000.0	468.2	466.8	467.5

Sodium Aluminium Alum.

The alum was made to crystallize from a water solution of its constituents by pouring a layer of alcohol upon the surface of the solution. With the gradual diffusion of the alcohol large, well-formed crystals of soda-alum, together with a few

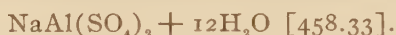
crystals of sodium sulphate appeared. When the mixture was washed quickly with cold water the small crystals of sodium sulphate dissolved, leaving the alum perfectly homogeneous throughout. Analysis of a standard solution gave :

I. 0.02402 gram $\text{NaAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

II. 0.02407 gram $\text{NaAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

Mean, 0.024047 gram alum per cc. equivalent to 0.05247 gram-molecules per litre.

Conductivity results are shown in the following table :



Gram-molecules per litre.	Litres per gram-molecule.	I. $\mu_v 25^\circ$.	II. $\mu_v 25^\circ$.	Mean.
0.05	20.0	161.5	161.6	161.6
0.025	40.0	184.4	184.7	184.6
0.005	200.0	250.0	251.2	250.6
0.0025	400.0	286.7	284.2	285.4
0.0005	2000.0	380.0	378.8	379.5
0.00025	4000.0	435.5	435.2	435.5

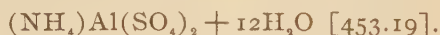
Ammonium Aluminium Alum.

After eleven crystallizations the salt was found to be free from sodium, but still retained a minute trace of potassium. The standard solution was analyzed by titration of the aluminium. The analysis gave the following results :

I. 0.04550 gram $(\text{NH}_4)\text{Al}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

II. 0.04585 gram $(\text{NH}_4)\text{Al}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

Mean, 0.04567 gram alum per cc., equivalent to 0.10076 gram-molecules per litre.



Gram-molecules per litre.	Litres per gram-molecule.	I. $\mu_v 25^\circ$.	II. $\mu_v 25^\circ$.	Mean.
0.1	10.0	152.8	152.9	152.8
0.05	20.0	174.5	175.0	174.8
0.025	40.0	198.1	198.4	198.2
0.005	200.0	261.4	260.6	261.0
0.0025	400.0	297.1	294.9	296.0
0.0005	2000.0	390.0	389.2	389.6
0.00025	4000.0	452.4	452.4	452.4
0.00005	20000.0	568.4	560.0	564.2
0.000025	40000.0	608.4	602.8	605.6

Potassium Chrome Alum.

The salt, purified by repeated crystallization from water at 35°, was dissolved and the solution standardized by precipitation of the sulphuric acid as barium sulphate. The analysis gave :

I. 0.11742 gram $\text{KCr}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

II. 0.11746 gram $\text{KCr}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

Mean, 0.11744 gram chrome alum per cc., equivalent to 0.2351 gram-molecules per litre.

Following are the results of conductivity measurements :

$\text{KCr}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ [499.53].

Gram-molecules per litre.	Litres per gram-molecule.	I. μ_{v25}° .	II. μ_{v25}° .	Mean.
0.1	10.0	147.8	148.1	147.9
0.05	20.0	170.5	170.3	170.4
0.025	40.0	195.4	195.0	195.2
0.005	200.0	266.7	266.5	266.6
0.0025	400.0	306.1	304.9	305.5
0.0005	2000.0	418.6	418.8	418.7
0.00025	4000.0	472.4	471.6	472.0

Ammonium Chrome Alum.

The salt was purified as in the case of the potassium chrome alum, and the solution standardized by precipitation of the sulphate. The analysis gave :

I. 0.09266 gram $(\text{NH}_4)\text{Cr}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

II. 0.09282 gram $(\text{NH}_4)\text{Cr}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

Mean, 0.09274 gram alum per cc., equivalent to 0.194 gram-molecules per litre.

The conductivity observed is shown in the following table :

$(\text{NH}_4)\text{Cr}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ [478.44].

Gram-molecules per litre.	Litres per gram-molecule.	I. μ_{v25}° .	II. μ_{v25}° .	Mean.
0.1	10.0	145.4	144.7	145.0
0.05	20.0	167.2	167.1	167.1
0.025	40.0	191.5	191.1	191.3
0.005	200.0	263.8	263.6	263.7
0.0025	400.0	304.0	303.6	303.8
0.0005	2000.0	••••	415.3	415.3
0.00025	4000.0	484.6	477.5	481.0

Green Modification of Ammonium Chrome Alum.

As is well known, solutions of chrome salts at a temperature between 70° and 80° lose their original color, passing to a green, and cease to have the power of depositing crystals. Recoura¹ has shown that the green modification is a well-defined basic salt mixed with free acid; and Monti² has found that the change is accomplished by a rise in conductivity. With a view to finding whether the passage to the green modification is discontinuous at any point, a series of qualitative experiments were made by placing the conductivity cell containing a solution of ammonium chrome alum in a bath, and regulating the heat so that the temperature rose uniformly with the time, noting at the same time, at regular intervals, the rise in conductivity. The latter showed no rapid rate of change, and it may be inferred that the passage to the green modification is a continuous change.

Ammonium Iron Alum.

A solution of the pure alum was standardized by titration of the reduced ferric salt with potassium permanganate, the reduction having been effected by a platinum-zinc couple. The results of analysis were:

I. 0.24772 gram $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

II. 0.24722 gram $(\text{NH}_2)\text{Fe}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc.

Mean, 0.24747 $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ per cc., equivalent to 0.5089 gram-molecules per litre.

Conductivity results are shown in the following table:

$(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ [482.24].		
Gram-molecules per litre.	Litres per gram-molecule.	$\mu_{v25^{\circ}}$.
0.25	4.0	118.9
0.05	20.0	177.4
0.025	40.0	211.5
0.005	200.0	320.2

Stability of Alums in Dilute Solutions.

In the course of the preceding measurements, it was noticed that the conductivities of dilute solutions of some of the alums

¹ Ann. chim. phys., [7], 4, 494, (1895).

² Ztschr. anorg. Chem., 12, 75. Refer., (April, 1896.)

increased at a more or less rapid rate on standing for a time. As such a change of conductivity must depend upon changed conditions in the solution, this observation indicates a different degree of stability in the presence of a large amount of water. Ammonium iron alum furnished the most marked instance of instability. At a dilution of 200 litres the conductivity of a solution of iron alum rose 3 per cent. in two hours. At 400 litres it showed the same increase in twenty minutes, and at a dilution of 2000 litres the rate of increase was about 1.2 per cent. per minute. This rate soon diminished and, at the end of twenty-four hours, an apparent state of equilibrium was reached after a total increase in conductivity of 30 per cent. At 0° a dilution of 1000 litres is reached before decomposition begins. The precipitate which accompanies the decomposition does not become visible until after the change in conductivity has become apparent. A rise in conductivity was also noticed in the case of soda alum and ammonium chrome alum, but not until a dilution of 20,000 liters was reached. The former at this dilution showed an increase of 4 per cent. in twenty-four hours. Similar examples of a rise in conductivity in dilute solutions have been noticed by Kohlrausch¹ in the case of barium nitrate, copper sulphate and other salts. In the former case it was clearly accompanied by the formation of a basic salt, and the liberation of free acid. In the case of chromium salts the rise in conductivity accompanying the formation of a basic salt has already been mentioned. The well-known tendency of ammonium iron alum to form basic salts is doubtless the cause of the change of conductivity noticed in its case. It seems probable, therefore, that a similar change occurs in very dilute solutions of soda and ammonium chrome alums brought about by the action of a large mass of water. Such a change would be analogous to that studied by Rose² in the case of acid potassium sulphate, which is decomposed by an excess of water forming the neutral sulphate and free acid.

Comparison of Conductivity Results.

If the foregoing conductivities of the alums be compared,

¹ Wied. Ann., 26, 175, (1885).

² Pogg. Ann., 82, 545, (1851).

it will be seen that throughout all dilutions they can be arranged in order of magnitude with respect to their conductivities from a knowledge of the conductivities of their constituents. The conductivities of potassium, sodium and ammonium sulphates are in the same order of magnitude as the conductivities of the corresponding alums.

A detailed comparison of the conductivities of the alums with the arithmetic means of the conductivities of their constituents is shown in the following tables. The data for the values of conductivity of aluminium sulphate have been derived from the table already given, supplemented by Walden's¹ results. The values given have been interpolated by the graphic method. The data for sodium sulphate are interpolated from Kohlrausch's² tables reduced to 25° and changed to molecular conductivity units. The values for potassium sulphate and chromium sulphate are taken directly without interpolation from the tables already given. No data for ammonium sulphate and ferric sulphate are available. As the latter only exists in acid solution, direct observations of its conductivity would have no value for the present purpose.

I. Potassium Aluminium Alum.

Litres per gram- molecule.	K ₂ SO ₄ . $\mu_{v25^{\circ}}$.	Al ₂ (SO ₄) ₃ . $\mu_{v25^{\circ}}$.	Arithmetic mean.	Alum, observed. $\mu_{v25^{\circ}}$.	Difference. Per cent.
5.0012	172.7	108.0	140.3	133.9	—4.5
8.0	183.3	124.2	153.7	149.2	—3.0
20.0	205.1	158.1	181.6	178.3	—1.7
40.0	220.3	185.7	203.0	202.5	—0.2
200.0	252.4	290.4	271.4	269.0	—0.8
400.0	262.2	342.6	302.4	305.2	+0.9

¹ Ztschr. phys. Chem., **1**, 541, (1887).

² Wied. Ann., **26**, 196, (1885).

II. Sodium Aluminium Alum.

Litres per gram- molecule.	Na_2SO_4 . μ_{v25° .	$\text{Al}_2(\text{SO}_4)_3$. μ_{v25° .	Arithmetic mean.	Alum, observed. μ_{v25° .	Difference. Per cent.
20.0	171.5	158.1	164.8	161.6	—1.9
40.0	183.1	185.7	184.4	184.6	+0.1
200.0	211.6	290.4	251.0	250.6	—0.2
400.0	219.1	342.6	280.8	285.4	+1.6

III. Potassium Chrome Alum.

Litres per gram- molecule.	K_2SO_4 . μ_{v25° .	$\text{Cr}_2(\text{SO}_4)_3$. μ_{v25° .	Arithmetic mean.	Alum, observed. μ_{v25° .	Difference. Per cent.
10.0	187.0	139.0	163.0	147.9	—9.2
20.0	205.1	162.7	183.9	170.4	—7.3
40.0	220.3	190.7	205.5	195.2	—5.0
200.0	252.4	288.2	270.3	266.6	—1.3
400.0	262.2	346.5	304.3	305.5	+0.4
2000.0	276.5	558.2	417.3	418.7	+0.3
4000.0	281.9	671.2	476.5	472.0	—0.9

A study of the preceding tables justifies the following statements:

(1) In concentrated solutions the conductivity of the alums is notably less than the mean of the conductivities of their constituents. (2) The defect of the conductivity from the mean is the same in amount for the aluminium alums, while it becomes much greater for chrome alum. (3) The difference between the conductivity of the alums and the mean conductivity of their constituents grows rapidly less with increasing dilution, so that at a dilution of 40 litres for the aluminium alums and of 400 for chrome alum it has disappeared.

Deductions from these facts must depend upon the relations which exist between the conductivity of a mixture of two electrolytes having a common ion and the conductivities of the constituents taken separately—assuming that the state

of the alum in solution is the same as if it had been formed by mixing equal volumes of solutions of its constituents having the same molecular concentration as itself. It has been shown, especially by the work of Bender¹ and Klein², that in such mixtures the conductivity is in general less than the mean of the conductivities of the constituent salts. But Klein showed that a more marked difference existed when the salts were capable of forming a double salt. Thus while potassium sulphate and sodium sulphate gave a difference of 1 per cent., potassium sulphate with ferrous sulphate gave for the same concentration 6 per cent. The differences found for the alums as given in the above table are of the same order ($2\frac{1}{2}$ to 11 per cent.) as those found by Klein for the double salts examined by him.

The condition that two electrolytes having a common ion may mix without undergoing a change in ionization, has been deduced from the dissociation theory of electrolytic conduction by Arrhenius.³ If no change of volume occurs on mixing, that condition is that the concentration of the ions, *i. e.*, the quotient of the coefficient of ionization divided by the volume containing one gram-molecule, shall be the same for the both solutions, or

$$\frac{\alpha_1 n_1 v_1}{v_1} = \frac{\alpha_2 n_2 v_2}{v_2}$$

where α_1 , α_2 , are the coefficients of ionization of the respective solutions; n_1 , n_2 , the number of gram-molecules contained respectively in a unit of volume of each; and v_1 , v_2 , the respective volumes of the solutions mixed.

The following table shows the extent to which this condition is fulfilled in some of the solutions of alums being studied. On the assumption already made, that we may regard a solution of the alum as having been formed by mixing equal volumes of solutions of its constituents of the same molecular concentration, n_1 and n_2 in the preceding equation become equal as also v_1 and v_2 , and it is only necessary to compare the values of α_1 and α_2 , for the constituent solutions. The values of α have been calculated from freezing-point data instead of from conductivity, since the experimental error in

¹ *Loc. cit.*

² *Loc. cit.*

³ *Ztschr. phys. Chem.*, 2, 284, (1888).

measuring μ_{∞} for aluminium sulphate and chromium sulphate may become very large. For potassium sulphate the two methods give concordant results, as is shown in the table given by Arrhenius.¹ In calculating the values of i , that is, the ratio between the observed and the normal osmotic pressure, the value 1.88 is taken for normal molecular-lowering. The corresponding values of α are calculated from the equation

$$i = 1 + (k-1) \alpha,$$

where k denotes the number of ions given by each active molecule, namely, 3 for potassium sulphate and 5 for aluminium sulphate.

Gram-molecules per litre.	K ₂ SO ₄		Al ₂ (SO ₄) ₃		Cr ₂ (SO ₄) ₃	
	i .	α .	i .	α .	i .	α .
0.117	2.22	0.61			2.20	0.30
0.1086	2.28	0.64	2.13	0.28		
0.1	2.30	0.65			2.21	0.30
0.098			2.21	0.30		
0.088	2.33	0.66			2.28	0.32
0.0653			2.34	0.33		
0.059	2.41	0.70			2.40	0.35
0.054	2.45	0.72				
0.05	2.44	0.72	2.44	0.38	2.44	0.38
0.0333	2.57	0.78				
0.0294	2.57	0.78			2.55	0.387
0.026			2.60	0.40		

It is seen that the values of α and, therefore, of $\frac{\alpha}{v}$, or the concentration of the ions for potassium sulphate, differ widely from those for either aluminium or chromium sulphate: while, for the latter sulphates, the values of α show an almost complete agreement throughout the range of dilution given. The change of dissociation or ionization produced by mixing with potassium sulphate should, therefore, be very nearly the same in both cases, if we neglect the effect of changes in volume which in this case are extremely small. Reference to the preceding tables I. and III., however, shows that this is by no means the case. The divergence from the mean is four or five times greater in the case of the chrome alum than for the aluminium alum at the same dilution, or, is also much greater if we compare them at equal distances from the point of satura-

¹ Ztschr. phys. Chem., 2, 491, (1887).

tion. Even if we conclude, therefore, that the potassium aluminium alum is entirely dissociated we must infer that the molecules of the double salt in a concentrated solution of chrome alum are only partially broken down. This conclusion with respect to chrome alum agrees with that reached on other grounds by Carey Lea,¹ who finds by the use of a reagent for the detection of free sulphuric acid in the presence of sulphates that chrome alum is the only one present as such in solution.

In order to find whether the solution of an alum is simply equivalent to a mixture of solutions of its equivalents, a number of mixtures were prepared of equal volumes of solutions of potassium sulphate and aluminium sulphate of the same molecular concentration and also of potassium sulphate and chromium sulphate. The conductivities of the constituents salts were observed, then that of the mixtures. The results appear in the following tables :

Potassium Sulphate and Aluminium Sulphate.

Gram-molecules per litre.	K_2SO_4 . μ_{v25° .	$Al_2(SO_4)_3$. μ_{v25° .	Mean.	Mixture observed. μ_{v25° .	Difference. Per cent.
0.2175	170.2	105.7	137.9	129.1	-6.4
0.10855	186.9	130.3	158.6	151.8	-4.3
0.05427	202.8	153.6	178.2	174.2	-2.2
0.03333	213.9	172.5	193.1	190.1	-1.6
0.01666	229.1	202.2	215.6	214.3	-0.6

Potassium Sulphate and Chromium Sulphate.

Gram-molecules per litre.	K_2SO_4 . μ_{v25° .	$Cr_2(SO_4)_3$. μ_{v25° .	Mean.	Mixture observed. μ_{v25° .	Difference. Per cent.
0.333	157.4	94.2	125.8	113.0	-10.1
0.25	167.9	107.3	137.6	125.1	-9.0
0.1	187.0	139.0	163.0	155.1	-4.9
0.05	205.1	162.7	183.9	177.9	-3.3
0.025	220.3	190.7	205.5	202.8	-1.3

¹ Ztschr. anorg. Chem., 4, 445, (1893).

The results for mixtures of potassium and aluminum sulphates show a close agreement with those obtained for the alum; those for potassium and chromium sulphates show a somewhat remarkable difference—the alum having a considerably lower conductivity at corresponding dilutions. It may be remarked that volume-changes play an unimportant part in this instance since, according to Gerlach's observations,¹ the contraction at 15° for a mixture of potassium and aluminum sulphates containing 0.21 gram-molecules per litre is 0.06 per cent., and for a mixture of potassium and chromium sulphates containing 0.27 gram-molecules per litre is at the same temperature 0.12 per cent. If the difference noticed is well founded, it might be accounted for by supposing that the molecules of the double salt remain in part undissolved when its crystals are dissolved, but that the molecules of the constituent salts do not necessarily unite when their solutions are mixed. This is the explanation given by Graham¹ of the fact observed by him that the diffusion of the double sulphate of potassium and magnesium differed from that of a mixture of its constituent salts.

Summary of Conductivity Results.

The preceding results in so far as they bear upon the existence of alums as such in solution may be summarized as follows:

1. The alums in dilute solution are entirely dissociated into their constituent salts.

2. In concentrated solution they have a lower conductivity than the mean conductivity of their constituents. The difference is more marked as the concentration increases; and is of the same order as that observed for other double sulphates, and greater than that observed in the case of mixtures of sulphates incapable of yielding a double salt. There is, therefore, some evidence that the alums are partially undissociated in concentrated solution.

3. The amount of the divergence from the mean conductivity of its constituents for chrome alum as compared with the aluminium alums affords strong evidence that this alum, at least, exists as such in solution.

¹ Ztschr. anal. Chem., 28, 505, (1889).

² Phil. Trans., 1850, 1.

Freezing-Point Measurements.

The apparatus used in the freezing-point observations was of the ordinary Beckmann form, except that the inner tube containing the solutions was slightly larger in diameter, to prevent the danger of the stirrer coming into contact with the thermometer, and had no side branch. The ice-bath was incased with felt. The solutions used were made up from the same solutions as those employed in conductivity work. In every freezing-point determination the same water was employed as that used in making up the solution in question.

The following tables show the freezing-point lowerings obtained for the alums and their constituent salts. The following symbols are used:

G denotes the number of grams of salt dissolved in a litre of solution.

N denotes the number of gram-molecules per litre of solution.

L denotes the corrected lowering.

Δ denotes the gram-molecular lowering.

In the case of the alums the double formulas are used for convenience in comparison with their constituents, the sum of the lowerings for the constituents being then directly comparable with the lowering of the alum.

I. K_2SO_4 [174.34].

No.	G.	N.	L.		No.	G.	N.	L.	Δ .
1	37.857	0.217	0.890°	4.10	1	58.1134	0.333	1.311°	3.93
2	18.9285	0.1086	0.466	4.29	2	43.5850	0.250	1.004	4.02
3	9.4643	0.0543	0.250	4.61	3	17.434	0.100	0.432	4.32
4	5.8110	0.0333	0.161	4.83	4	8.717	0.050	0.230	4.60
5	2.9055	0.0167	0.084	5.03	5	4.3585	0.025	0.122	4.88

II. $Al_2(SO_4)_3$ [342.34].

No.	G.	N.	L.		No.	G.	N.	L.	Δ .
1	44.740	0.131	0.516°	3.94	1	74.338	0.217	0.832°	3.83
2	33.555	0.098	0.410	4.18	2	37.169	0.1086	0.438	4.03
3	22.370	0.0653	0.288	4.41	3	18.5845	0.0543	0.245	4.51
4	15.659	0.0457	0.212	4.64	4	11.411	0.0333	0.189	4.77
5	8.948	0.0261	0.127	4.87	5	5.7055	0.0166	0.088	5.30
6	6.711	0.0196	0.101	5.15					
7	4.474	0.0131	0.073	5.57					

III. $\text{Cr}_2(\text{SO}_4)_3$ [392.58].

No.	G.	N.	L.	Δ .
1	130.860	0.333		
2	98.145	0.250	1.029°	4.12
3	39.258	0.100	0.417	4.17
4	19.629	0.05	0.230	4.60
5	9.8145	0.025	0.121	4.84

IV. $(\text{NH}_4)_2\text{SO}_4$ [132.16].

No.	G.	N.	L.	Δ .
1	26.432	0.2	0.829°	4.145
2	13.216	0.1	0.437	4.370
3	9.2512	0.07	0.316	4.514
4	6.608	0.05	0.237	4.740
5	3.9648	0.03	0.148	4.933
6	1.9824	0.015	0.075	5.00

V. $\text{K}_2\text{Al}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$ [948.82].

No.	G.	N.	L.	Δ .
1	47.441	0.05	0.409°	8.18
2	35.5807	0.0375	0.320	8.53
3	23.720	0.025	0.222	8.88
4	11.8575	0.0125	0.120	9.60
5	4.7430	0.005	0.057	11.40

VI. $\text{Na}_2\text{Al}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$ [916.66]

No.	G.	N.	L.	Δ .
1	22.9165	0.025	0.229°	9.16
2	11.4582	0.0125	0.125	10.00
3	5.7291	0.00625	0.009	11.04

VII. $(\text{NH}_4)_2\text{Al}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$ [906.6].

No.	G.	N.	L.	Δ .
1	45.330	0.05	0.408°	8.16
2	33.997	0.0375	0.318	8.48
3	22.665	0.025	0.224	8.96
4	11.332	0.0125	0.121	9.68
5	5.666	0.00625	0.066	10.56

VIII. $\text{K}_2\text{Cr}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$ [999].

No.	G.	N.	L.	Δ .
1	117.44	0.117	0.888°	7.59
2	88.08	0.088	0.686	7.80
3	58.72	0.059	0.480	8.14
4	29.36	0.0294	0.267	9.08
5	17.618	0.0176	0.170	9.66
6	11.744	0.0117	0.119	10.17
7	5.872	0.0059	0.065	11.02

IX. $(\text{NH}_4)_2\text{Cr}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$ [256.8].

No.	G.	X.	L.	J.
1	92.740	0.007	0.768 ⁷	7.92
2	46.370	0.0484	0.400	8.26
3	27.822	0.0201	0.266	9.14
4	16.6932	0.0174	0.168	9.65
5	11.1288	0.0116	0.117	10.00
6	5.5644	0.0058	0.064	11.04

X. $(\text{NH}_4)_2\text{Fe}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$ [304.42].

No.	G.	X.	L.	J.
1	247.72	0.257	1.820 ⁹	7.08
2	123.86	0.192	1.400	7.20
3	82.57	0.128	0.927	7.24
4	61.930	0.096	0.713	7.43
5	41.286	0.064	0.505	7.80
6	30.642	0.0385	0.322	8.36
7	24.772	0.0257	0.227	8.83
8	16.386	0.0128	0.121	9.43
9	10.23	0.0064	0.060	10.31

Comparison of Freezing-Point Results.

Comparing the results for the different alums as shown in the foregoing tables, it will be seen that, as regards the aluminium alums, the soda alum (Table VI) gives a greater depression for corresponding dilutions than either potassium (Table V) or ammonium alum (Table VII), while the depressions given by potassium alum correspond closely, but are slightly larger in concentrated solution than those for the ammonium alum. For dilute solutions the reverse is the case, but the experimental error is here greater and less value is to be attached to the results. The ammonium chrome and potassium chrome alums also show closely corresponding values for corresponding dilutions (Tables VIII, IX), while these values are somewhat greater for corresponding dilutions than those of the aluminium alums.

In the following tables is shown a comparison of the lowerings given by the alums with the sum of the lowerings for their constituents at the same dilution. The values for the constituent salts are interpolated from the preceding tables I to IV.

Potassium Aluminium Alum.

No.	N.	K_2SO_4 Δ .	$Al_2(SO_4)_3$ Δ .	Sum.	Potassium alum. Δ observed.	Differ- ence.
1	0.05	4.61	4.60	9.21	8.18	1.03
2	0.0375	4.76	4.72	9.48	8.53	0.95
3	0.025	4.89	4.91	9.80	8.88	0.92
4	0.0125	5.02	5.61	10.63	9.60	1.03

Ammonium Aluminium Alum.

No.	N.	$(NH_4)_2SO_4$ Δ .	$Al_2(SO_4)_3$ Δ .	Sum.	Amm.-Al. alum. Δ observed.	Differ- ence.
1	0.05	4.74	4.55	9.29	8.15	1.13
2	0.0375	4.86	4.72	9.58	8.48	1.10
3	0.025	4.95	4.01	9.86	8.96	0.90
4	0.0125	5.02	5.61	10.63	9.68	0.95

Potassium Chrome Alum.

No.	N.	K_2SO_4 Δ .	$Cr_2(SO_4)_3$ Δ .	Sum.	K-Cr alum. Δ observed.	Differ- ence.
1	0.117	4.28	4.16	8.44	7.59	0.85
2	0.088	4.38	4.27	8.65	7.80	0.85
3	0.059	4.54	4.51	9.05	8.14	0.91
4	0.0294	4.83	4.80	9.63	9.07	0.55

Ammonium Chrome Alum.

No.	N.	$(NH_4)_2SO_4$ Δ .	$Cr_2(SO_4)_3$ Δ .	Sum.	Amm.-Cr alum. Δ observed.	Differ- ence.
1	0.097	4.38	4.19	8.57	7.92	0.65
2	0.0484	4.76	4.61	9.37	8.26	1.11
3	0.0291	4.93	4.81	9.74	9.14	0.60

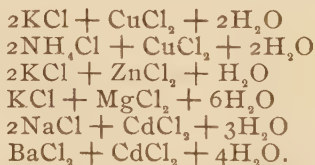
These tables show that for the most concentrated solutions the lowerings given by the alums, with the exception of ammonium chrome alum, is uniformly 10 or 11 per cent. less than the sum of the lowerings for its components. The abnormal

value for ammonium chrome alum—giving 7.3 per cent.—may be attributed to experimental error, since the other values obtained for it are in agreement with those of the other alums. Raoult¹ found for potassium aluminium alum a lowering of 1.2 per cent. less than the sum of those obtained for its components, and he inferred that its dissociation was complete. He does not, however, state the concentration observed; and the extent to which the difference obtained depends upon concentration is apparent from the above table. These results must be regarded as confirming the indications given by conductivity of the existence of alum molecules in concentrated solution.

II.

Double Chloride of Zinc and Potassium.

Rüdorff² distinguished, as has already been mentioned, two classes of double chlorides. (1) those which suffer decomposition in water solution, and (2) those which remain undecomposed. The first class are to be regarded as double salts of the same type as the alums. The second class he regards as true binary compounds. The following examples of the first class are given :



It seemed of interest in connection with the foregoing investigation to study an example of this class by the conductivity method. For this purpose, the double chloride of potassium and zinc, $2\text{KCl} \cdot \text{ZnCl}_2 + \text{H}_2\text{O}$ was selected.

Preparation.

In preparing the double chloride of potassium and zinc, potassium chloride was used which had been twice crystallized, and was shown by the flame test to be free from sodium. The zinc chloride used was tested and found free

¹ Compt. rend., 99, 914, (1884).

² Ber. d. chem. Ges., 21, 3048, (1888).

from impurities. The two chlorides were brought together in solution in the proportion necessary to form the double salt, and the solution evaporated to crystallization. The salt was separated as rapidly as possible from its mother-liquor on the filter-pump, and dried under a press. A specimen, previously dried at 130° , was immediately weighed off, and analyzed for zinc.

The analysis gave :

Percentage of zinc found 22.91

“ “ calculated for $2\text{KCl} \cdot \text{ZnCl}_2$. 22.94

The solution was standardized by precipitating zinc by sodium carbonate and weighing as zinc oxide.

The conductivity results are tabulated below :

$2\text{KCl} \cdot \text{ZnCl}_2$ [285.58].

Gram- molecules per litre.	Litres per gram- molecule.	I. $\mu_v 25^{\circ}$.	II. $\mu_v 25^{\circ}$.	Mean.
0.2	0.5	117.2		117.2
0.1	1.0	176.0		176.0
0.5	2.0	244.2		244.2
0.25	4.0	303.7		303.7
0.05	20.0	397.4	397.2	397.3
0.025	40.0	426.2	423.8	425.3
0.005	200.0	468.4	469.0	468.7
0.0025	400.0	483.2	484.2	483.7
0.0005	2000.0	504.0	504.6	504.3
0.00025	4000.0	510.8	512.3	511.5
0.00005	20000.0	516.8	509.0	512.9
0.000025	40000.0	518.8	516.0	517.4

A comparison of the conductivity of the double salt with the conductivities of its constituents is given below. The values for zinc chloride and potassium chloride are interpolated from the tables of Kohlrausch¹ and reduced to 25° . The molecular conductivity of the zinc chloride is taken at the same volume as the double salt. That of potassium chloride is taken as twice the molecular conductivity of potassium chloride at one-half the volume of the double salt.

¹ Wied. Ann. 26, 161, (1885).

Double Chloride of Zinc and Potassium.

Litres per gram-mole- cule of KCl.	KCl. $2 \times \mu_{25^\circ}$.	Litres per gram-mole- cule of ZnCl_2 .	ZnCl_2 . μ_{25° .	Sum.	$2\text{KCl} \cdot \text{ZnCl}_2$ observed. μ_{25° .	Differ- ence.
0.5	196.0	0.1	78.4	274.4	176.0	98.4
1.0	211.8	2.0	120.0	331.8	244.2	87.6
2.0	221.6	4.0	140.3	361.9	303.7	58.2
10.0	241.4	20.0	179.2	420.6	397.3	23.3
20.0	250.0	40.0	186.7	436.7	425.3	11.4
100.0	264.8	200.0	213.6	478.4	468.7	9.7
200.0	269.0	400.0	220.1	489.1	483.7	5.4
1000.0	275.4	2000.0	232.0	507.4	504.3	3.1
2000.0	277.6	4000.0	234.8	512.4	511.5	0.9
10000.0	279.0	20000.0	240.2	519.2	512.9	6.3
20000.0	280.0	40000.0	240.7	520.7	517.4	3.3

The foregoing comparison leaves no room for doubt as to the existence of this double salt as such in concentrated solution, while at a dilution of between 1000 and 2000 liters it is entirely dissociated into its constituents.

Conclusion.

Regarding the double chloride of zinc and potassium as a type of the class of dissociated double haloids, we may draw the conclusion that these salts are present as such in their concentrated solutions. As compared with the alums, they show a greater degree of stability towards water in concentrated solutions, but, in dilute solutions, resemble them in becoming wholly dissociated into their component salts.

BIOGRAPHICAL.

The author is a native of Plainfield, Nova Scotia, where he was born January 24, 1864. He graduated as Bachelor of Arts from Dalhousie College, Halifax, N. S., in 1886, and thereafter occupied a position as a teacher in the High School, New Glasgow, N. S., until 1892. In October, 1892, he entered the Johns Hopkins University, where he has since been pursuing a post-graduate course in Chemistry, Physics, and Mathematics. He was awarded a University scholarship in Chemistry in January, 1895, and was appointed a Fellow in June of the same year.

